Polymer 147 (2018) 202–212

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Structural analyses of sphere- and cylinder-forming triblock copolymer thin films near the free surface by atomic force microscopy, X-ray photoelectron spectroscopy, and grazing-incidence small-angle X-ray scattering

Rasha Ahmed Hanafy Bayomi [a, b], Takashi Aoki [a], Takuma Shimojima [a], Hideaki Takagi [c], Nobutaka Shimizu [c], Noriyuki Igarashi [c], Sono Sasaki [a], Shinichi Sakurai [a, d, *]

[a] *Department of Biobased Materials Science, Graduate School of Science and Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*
[b] *Department of Apparel Design and Technology, Faculty of Applied Arts, Helwan University, Orman, Giza 12111, Egypt*
[c] *Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan*
[d] *Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

ARTICLE INFO

Article history:
Received 23 February 2018
Received in revised form
2 May 2018
Accepted 29 May 2018
Available online 31 May 2018

Keywords:
Block copolymer
Spherical microdomain
Cylindrical microdomain
Surface structure
Thin film
Atomic force microscopy
X-ray photoelectron spectroscopy
Grazing-incidence small-angle X-ray scattering

ABSTRACT

We investigated surface structures of three kinds of block copolymer (BCP) specimens forming hard spherical microdomains embedded in a soft matrix, by using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and grazing-incidence small-angle X-ray scattering (GISAXS). The three BCP specimens consist of different chemical species such as SEBS (polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene) and MAM (polymethylmethacrylate-*block*-poly(*n*-butylacrylate)-*block*-polymethylmethacrylate). Two of them form spherical microdomains at the thermodynamically equilibrium state (i.e., after fully long time thermal annealing), while the other exhibits spherical microdomains as a frozen state of the non-equilibrium structure (i.e., at the as-cast state using a selective solvent for the solution casting method), which was automatically frozen in by the vitrification of the hard component; the state is far from equilibrium). Nevertheless, such three different BCP specimens (chemically different in the molecular structure and thermodynamically different in the state) showed a common feature of the surface structure, as the outermost surface was completely covered with the single component having a lower value of the surface free energy, as revealed by XPS measurements. This finding significantly indicates that the AFM observation, which implies a coexistence of both BCP components on the free surface, misleads the conclusion. Although such surface coverage is reasonable and well-known, it was further found that the block chains are confined in a thin layer of the outermost region of the specimen. It is striking to find that the block chains are forced to be deformed (compressed) in order to meet the thermodynamic requirement of the surface coverage.

1. Introduction

Surface-related phenomena and properties of materials such as wetting/dewetting, permeation of gas or liquid molecules, antifouling, antiweatherability, anticoagulation, and so forth can be mainly controlled by the surface, of which thickness is only less than ~100 nm. This corresponds to a part less than 0.1% of a membrane material if its thickness is 0.1 mm. In other words, surface-related phenomena and properties can only be governed by such minor component existing in the surface range, and the remained part contributes to the robustness of the material. Therefore, it is very important to fabricate surface structures.

Block copolymer (BCP) surfaces may have utility in many applications such as biomaterials, medical implants, and tissue engineering. It has been reported that a microphase-separated PS-*b*-PMMA (polystyrene-*block*-polymethylmethacrylate) substrate can be used as a guide of selective adsorption of proteins such as immunoglobulin, bovine serum albumin, and fibrinogen [1–5].

---

* Corresponding author.
E-mail address: shin@kit.ac.jp (S. Sakurai).

https://doi.org/10.1016/j.polymer.2018.05.074

More interestingly, a larger amount of adsorption has been found on that BCP substrate as compared to the case of using the substrate composed of the random copolymer that comprises the same components of the BCP [5]. It is stated in these literature that preferred surface adsorption of proteins is due to hydrophobicity [1–5]. Namely, if regular structures are formed in the surface range of a BCP substrate, a periodic pattern of changing hydrophobicity can be created. However, this opinion may conflict with the thermodynamic requirement that the outermost surface of the BCP substrate should be completely covered with the single component having a smaller surface free energy. Indeed, Russell et al. [6] and Tanaka et al. [7] have presented very clear experimental evidence that the outermost surface is completely covered with PS for the PS-*b*-PMMA substrate and for phase-separated PS/PMMA blend (for which the thickness of the specimen is 25 μm, not so thin as 100 nm), even though the surface free energy for PS and that for PMMA are closer to each other (see Table 2). Another important experimental finding by Kumar et al. [2] is that the amount of adsorbed proteins is larger for the PS-*b*-PMMA substrate as compared to the case of using the PS homopolymer substrate. This suggests that there is another governing factor for the protein adsorption, which may be the surface undulation. Although the authors reported about 1 nm roughness of the free surface as evaluated by atomic force microscopy (AFM), this effect was not severely taken into account [2]. However, the fibrinogen molecule (5–7 nm diameter with 45–55 nm length) can fit such a wavy surface with 1 nm height difference. As a matter of fact, the surface topology of the BCP substrate and the positions of adsorbed fibrinogen molecules exactly match each other [4]. Therefore, it is considered that the regularly undulating surface of the BCP substrate can stabilize the fibrinogen molecules by placing them on the concave portions of the undulating surface. The reason why this promising effect has been ignored is due that the AFM result misled the surface structures (misleading coexistence of both component phases on the free surface). Therefore, this can be a clear example showing the significance of characterizing the outermost surface of BCP substrates, which is one of the main subjects of the current study.

Many different experimental techniques have been used to analyze the surface structures, such as transmission electron microscopy (TEM), scanning electron microscopy, AFM, grazing incidence small-angle X-ray scattering (GISAXS), X-ray and neutron reflectivity measurements, X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy, and attenuated total reflection measurement of Fourier transform infrared spectroscopy. Among them, XPS technique is special as it can analyze the components existing in the outermost surface region less than 10 nm from the free surface. Therefore, this method has been used to examine whether the outermost surface of polymer alloy (polymer blend/block copolymer) is covered with the component bearing a smaller surface free energy value at the thermodynamical equilibrium state [8]. The existence of a very thin layer at the free surface can be confirmed by XPS, although regular undulation of the free surface of the BCP film was clearly observed by AFM [9]. It would be considered that such selective surface coverage can be detected by a phase image of the tapping mode AFM observation for a specimen containing components with different hardness. However, such selection of the surface coverage cannot be detected by the tapping mode AFM as it visualizes the coexistence of the soft and hard phases even for the BCP substrate having a very thin layer covering its free surface. This fact indicates disability of the AFM method for detection of the thin layer existing at the outermost surface of the specimen. The XPS method can detect the existence of such a very thin layer.

The TEM method is also a powerful technique to detect the surface layer. Hasegawa et al. have reported clear TEM images for the surface thin layers covering the free surfaces of BCP specimens forming lamella [8,10], cylinder [8,11], gyroid [8] (the authors referred the morphological state as a tetrapod-network structure in the literature), and sphere [8]. Especially, it is striking that even for the BCP specimen forming spherical microdomains they succeeded to observe with TEM that the minor component can cover the free surface by forming a very thin layer [8] Although these findings are good accord with the thermodynamic requirement to reduce the surface free energy at the free surface, Kawaguchi at el. reported coexistence of two components on the free surface of the diblock copolymer forming a lamellae structure [12]. The diblock copolymer utilized is so special that the two components have similar surface free energy values and bulky side-chains. They attributed the coexistence of the two components on the surface to the tendency of the bulky side-chains preferring segregation to the surface. It is stated further that due to this effect the perpendicular orientation of the lamellar structures was attained [12].

In the current paper, we provided detailed XPS, AFM, and GISAXS results and based on them plausible models are constructed for nano-scaled structures at the outermost surface of BCP specimens forming hard spherical microdomains or hard cylindrical microdomains (oriented perpendicular to the surface), which are embedded in a soft matrix. Exploration of two-dimensional microdomain arrangement near the free surface is another

Table 1
Molecular characteristics of samples, the glass transition temperature, and the unperturbed radius of gyration for the soft and hard components.

Sample code	M_n	M_w/M_n	ϕ_{minor}	T_g (°C)		$\left\langle \mathbf{R}_g^2 \right\rangle_0^{1/2}$ (nm)	
				soft (by DSC)	hard	soft bridge confor-mation	hard
SEBS-8	6.7×10^4	1.04	0.084	−61.6	60.6 [35]	8.49	2.24
SEBS-16	6.6×10^4	1.03	0.16	−60.3	55.9 [35]	8.07	3.03
MAM	7.4×10^4	1.15	0.22	−46.8	85 [a]	6.32	3.72

M_n: Number-average molecular weight.
M_w: Weight-average molecular weight.
ϕ_{minor}: The volume fraction of PS in SEBS and PMMA in MAM.
T_g: The glass transition temperature for the soft components (PEB or PnBA) and for the hard components (PS or PMMA).
$\left\langle \mathbf{R}_g^2 \right\rangle_0^{1/2}$: The root-mean-square of the unperturbed radius of gyration for the soft components (PEB or PnBA) and the hard components (PS or PMMA), estimated from the characteristic ratio ($\left\langle R^2 \right\rangle_0 / M$) for PEB [39], PS [39], and PMMA [39]. $\langle R^2 \rangle_0$ is the mean-square unperturbed end-to-end distance of the polymer chain, and M is the molecular weight. As for PnBA, there is no literature value. However, the values for polymethylacrylate [40], polyethylacrylate [40], and polyisopropylacrylate [40] are available. Therefore, by extrapolating the value for PnBA is estimated as $\left\langle R^2 \right\rangle_0 / M = 3.7 \times 10^{-3}$ nm^2.

[a] Estimated from the molecular weight dependency of T_g as $T_g = 125.6 - 3.40 \times 10^5 / M_n$ (°C) for PMMA with the tacticity mm% = 0, mr% = 36, and rr% = 64 [38].